BEST AVAILABLE IMAGES

Defective images within this document are accurate representations of the original documents submitted by the applicant.

Defects in the images may include (but are not limited to):

- BLACK BORDERS
- TEXT CUT OFF AT TOP, BOTTOM OR SIDES
- FADED TEXT
- ILLEGIBLE TEXT
- SKEWED/SLANTED IMAGES
- COLORED PHOTOS
- BLACK OR VERY BLACK AND WHITE DARK PHOTOS
- GRAY SCALE DOCUMENTS

IMAGES ARE BEST AVAILABLE COPY.

As rescanning documents *will not* correct images, please do not report the images to the Image Problem Mailbox.

IN THE UNITED STATES PATENT AND TRADEMARK OFFICE

In re application of	:	
Jurgen VAN HOLEN	:	
Serial No. NEW	:	**Attn: APPLICATION BRANCH**
Filed April 12, 2004	:	Attorney Docket No. 2004_0529A

PROCESS USING A CYCLIC CARBONATE REACTANT AND β-HYDROXYURETHANES THEREBY OBTAINED

CLAIM OF PRIORITY UNDER 35 USC 119

Commissioner for Patents
P.O. Box 1450
Alexandria, VA 22313-1450

Sir:

Applicant in the above-entitled application hereby claims the date of priority under the International Convention of European Patent Application No. 03009307.4, filed April 24, 2003, as acknowledged in the Declaration of this application.

A certified copy of said European Patent Application is submitted herewith.

Respectfully submitted,

Jurgen VAN HOLEN

By _____
Matthew M. Jacob
Registration No. 25,154
Attorney for Applicant

MJ/da
Washington, D.C. 20006-1021
Telephone (202) 721-8200
Facsimile (202) 721-8250
April 12, 2004

Europäisches Patentamt	European Patent Office	Office européen des brevets

Bescheinigung | Certificate | Attestation

Die angehefteten Unterlagen stimmen mit der ursprünglich eingereichten Fassung der auf dem nächsten Blatt bezeichneten europäischen Patentanmeldung überein.

The attached documents are exact copies of the European patent application described on the following page, as originally filed.

Les documents fixés à cette attestation sont conformes à la version initialement déposée de la demande de brevet européen spécifiée à la page suivante.

Patentanmeldung Nr. | Patent application No. | Demande de brevet n°

03009307.4

Der Präsident des Europäischen Patentamts;
Im Auftrag

For the President of the European Patent Office

Le Président de l'Office européen des brevets
p.o.

R C van Dijk

Anmeldung Nr:
Application no.: 03009307.4
Demande no:

Anmeldetag:
Date of filing: 24.04.03
Date de dépôt:

Anmelder/Applicant(s)/Demandeur(s):

UCB, S.A.
Allée de la Recherche 60
1070 Bruxelles
BELGIQUE

Bezeichnung der Erfindung/Title of the invention/Titre de l'invention:
(Falls die Bezeichnung der Erfindung nicht angegeben ist, siehe Beschreibung.
If no title is shown please refer to the description.
Si aucun titre n'est indiqué se referer à la description.)

Process using a cyclic carbonate reactant

In Anspruch genommene Priorität(en) / Priority(ies) claimed /Priorité(s) revendiquée(s)
Staat/Tag/Aktenzeichen/State/Date/File no./Pays/Date/Numéro de dépôt:

Internationale Patentklassifikation/International Patent Classification/ Classification internationale des brevets:

C07C269/00

Am Anmeldetag benannte Vertragstaaten/Contracting states designated at date of filing/Etats contractants désignées lors du dépôt:

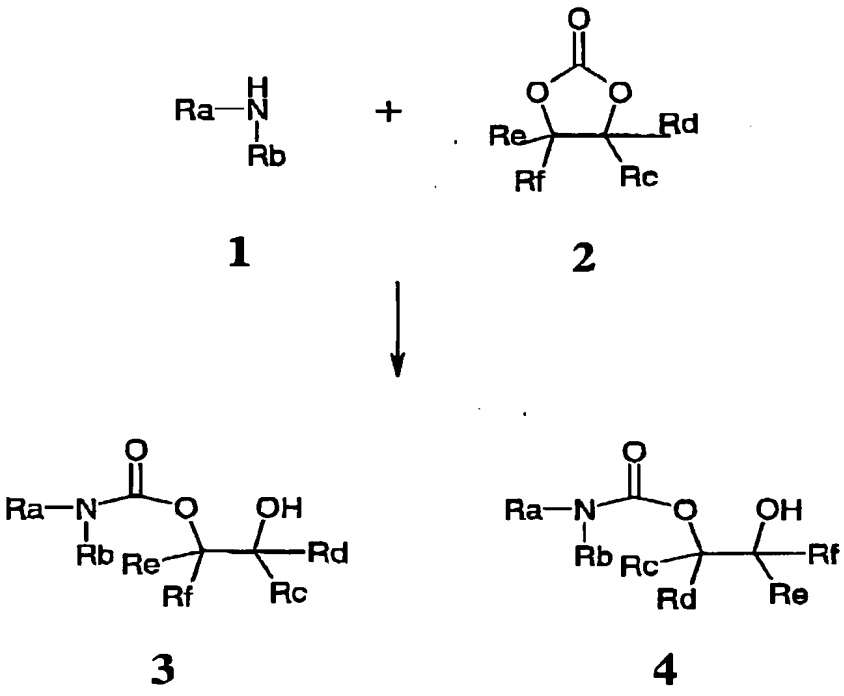
AT BE BG CH CY CZ DE DK EE ES FI FR GB GR HU IE IT LU MC NL PT RO SE SI SK TR LI

Process using a cyclic carbonate reactant

The present invention relates to a process wherein an electrophilic group containing cyclic carbonate compound is reacted with a compound containing a nucleophilic function. It also relates to the synthesis of the electrophilic group containing cyclic carbonate compound.

The reaction of a cyclic carbonate compound with a compound containing a nucleophilic group, especially an amine compound, is known. First publications on that subject date from late fifties early sixties: see for example US 2,802,022, US 2,935,494 and US 3,072,613.

When an amine compound (1) is reacted with a cyclic carbonate compound containing a 5-membered ring (1,3-dioxolan-2-one ring) (2), the product obtained is a betahydroxyurethane (3 and/or 4):



Urethane groups are useful in polymer preparation, such as polyurethanes, or other urethane-containing polymers.

Compared to ordinary urethane groups, betahydroxyurethane groups can provide desirable properties to the formed polymer, namely:

- the increased resistance towards hydrolysis (Figovski.O., Improving the protective properties of non metallic corrosion resistant materials and coatings. Journal of Medeleev Chemical Society. N.Y., USA 1988 Vol 33 No 3 .pp 31-36)
- more hydrophilic polymers

- the extra functional groups make it possible to afterwards crosslink the polymer if desired

Another advantage of the reaction between amine and cyclic carbonate compounds is that it allows preparation of polyurethane polymers without isocyanate reactants. Such polymers are often called "non-isocyanate" polyurethane polymers. Although the use of di-isocyanates for the synthesis of polyurethanes is widely accepted throughout the industry, there are some disadvantages connected with the NCO chemistry:

- di-isocyanates are toxic and need special care while handled
- di-isocyanates with a low vapour pressure can be absorbed easily by the human body (skin, eyes, lungs) and are to be considered as very hazardous chemicals
- their production involves phosgene while HCl is emitted: this process requires extreme safety measures
- because of the hydrogenation step and the consequent purification, aliphatic di-isocyanates are expensive and often prevent the use of polyurethanes in a given application for economical reasons.

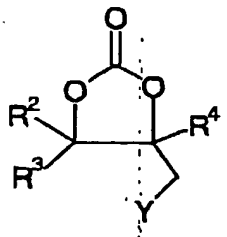
However, cyclic carbonates react relatively slowly with amines, particularly hindered primary or secondary amines and at ambient (about 25.degree. C.) temperatures. This slow reactivity has limited the usefulness of these types of reactions, for example in coatings which crosslink at ambient temperature. Therefore, means of speeding up such reactions is desired.

A great number of catalysts speeding up such reactions have been already described in literature. For example, US 5,055,542 and US 5,132,458 recommend the use of strongly basic compounds as catalysts for reaction including less reactive secondary amines. Such a strongly basic compound is, for example, diazabicyclooctane (DABCO). So-called supranucleophilic catalysts, for example 4-pyrrolidinopyridine are also suitable here. US 5,977,262 recommends the use of potassium tert-butoxide as catalyst.

However, known catalysts are either not very effective (ammoniumsalts) and/or not suited for an industrial process (very strong bases such as potassium tert-butoxide). Moreover, some reagents (amines) are not compatible with the strong bases. On the other hand, without a catalyst the reaction takes several days.

The present invention provides a process of forming an organic compound, wherein

(a) a component (A) containing at least one cyclic carbonate group having the general formula (I):



(I)

R^2, R^3 and R^4 are, independently, chosen from: hydrogen, aromatic radical, alkyl or alkenyl which contains from 0 to 8 ether bridges, and R^2 and/or R^3 and/or R^4 may be substituted by one or more alkyl, alkenyl, aromatic radical, hydroxyl group(s), cyclic carbonate group of formula (I), and wherein Y is an electrophilic group selected from ammonium and phosphonium, eventually substituted by alkyl groups themselves eventually substituted by an aromatic radical, and wherein each R^2 and/or R^3 and/or R^4 may be replaced by an Y group.

(b) is reacted with a component (B) containing at least one reactive nucleophilic function X wherein each X is, independently, chosen from a primary amino or hydrazo, secondary amino or hydrazo, thiol, hydroxy, and/or oxime,

(c) to form an organic compound (C) containing at least one unit of the general formula (III): -X-CO-O-.

It has now surprisingly been found that the presence of at least one electrophilic group containing radical Y, attached to the cyclic carbonate through a methylene bridge, greatly enhance the reaction rate between this cyclic carbonate and a compound [B] containing a reactive nucleophilic function X, such as an amine function for example.
The reaction is sufficiently fast, which means that the reaction can be achieved at room temperature.

By component (B) containing a reactive nucleophilic function X which is a primary amino is meant any compound bearing a $-NH_2$ group attached directly to a carbon atom.
By component (B) containing a reactive nucleophilic function X which is a secondary amino is meant any compound bearing a –NH group attached directly to 2 carbon atoms.
By component (B) containing a reactive nucleophilic function X which is a thiol is meant any compound bearing a –SH group attached directly to a carbon atom.
By component (B) containing a reactive nucleophilic function X which is an hydroxy is meant any compound bearing a –OH group attached directly to a carbon atom.
By component (B) containing a reactive nucleophilic function X which is an oxime is meant any compound bearing a =N-OH group attached directly to a C atom.
The term "alkyl", as used herein, is defined as including saturated, monovalent hydrocarbon radicals having straight, branched or cyclic moieties or combinations thereof and containing 1 to 50 carbon atoms.

The term "alkenyl" as used herein, is defined as including straight and cyclic, branched and unbranched, unsaturated hydrocarbon radicals having at least one double bond and containing from 2 to 50 carbon atoms; such as ethenyl (= vinyl), 1-methyl-1-ethenyl, 2-methyl-1-propenyl, 1-propenyl, 2-propenyl (= allyl), 1-butenyl, 2-butenyl, 3-butenyl, 4-pentenyl, 1-methyl-4-pentenyl, 3-methyl-1-pentenyl, 1-hexenyl, 2-hexenyl, and the like.

The term "aryl" as used herein, is defined as including an organic radical derived from an aromatic hydrocarbon comprising 1 or more rings by removal of one hydrogen, and containing from 5 to 30 carbon atoms, such as phenyl and naphthyl.

The term "aromatic radical" as used herein, is defined as comprising a combination of alkyl or alkenyl and aryl, such as benzyl.

The term "alkylene" as used herein, is defined as including saturated, divalent hydrocarbon radicals having straight, branched or cyclic moieties or combinations thereof and containing 1 to 50 carbon atoms.

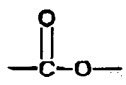
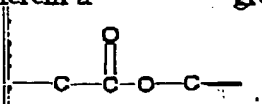
The term "alkenylene" as used herein, is defined as including unsaturated, divalent hydrocarbon radicals having straight, branched or cyclic moieties or combinations thereof, containing at least one carbon-carbon double bond and containing 1 to 50 carbon atoms.

The term "arylene" as used herein, is defined as including divalent radicals derived from an aromatic hydrocarbon comprising one or more rings by removal of two hydrogen atoms and containing from 5 to 30 carbon atoms.

The term "aralkylene" as used herein, represents a divalent radical comprising a combination of alkylene and arylene moieties.

By alkyl, alkenyl, alkylene, alkenylene, arylene and aralkylene containing an ether bridge is meant an alkyl, alkenyl, alkylene, alkenylene, arylene or aralkylene radical wherein a carbon atom is replaced by an oxygen atom, forming a group such as –C-O-C-.

By alkyl, alkylene, alkenylene, arylene and aralkylene chain containing tertiary amine bridge is meant such radical wherein a tertiary amine group is present between 2 carbon atoms, forming a group of formula –C-NR-C-, wherein R represents an alkyl or aryl group. In that case, R is preferably an alkyl group containing from 1 to 15 carbon atoms.

By alkylene, alkenylene, arylene and aralkylene containing a -CO-O- bridge is meant an alkylene, alkenylene, arylene or aralkylene radical wherein a  group is present between 2 carbon atoms, forming a group of formula  .

By alkylene, alkenylene, arylene and aralkylene containing a -CO- bridge is meant an alkylene, alkenylene, arylene or aralkylene radical wherein a  group is present between 2 carbon atoms.

By electrophilic group Y is meant such functional groups as ammonium $(R^1)3N+$ or phosphonium, $(R^1)3P+$ groups, eventually substituted by alkyl groups R^1. These alkyl groups may be themselves substituted by aromatic radicals, as defined herein. The electrophilic group Y is linked to the cyclic carbonate group through a methylene group.

Advantages obtainable by the claimed process include :

- An increase of reaction speed during the synthesis of (poly)urethanes by reacting (poly)amines with (poly)cyclocarbonates.
- Cheap, commercially available (poly)amines can be used for the synthesis of (poly)urethanes. These amines include JEFFAMINE, diethanolamine, piperazine....
- Because the reaction speed is increased considerably, even hindered primary and secondary amines can be used in the synthesis.
- Shorter reaction times and lower curing temperatures also lead to an economical advantage.

Preferably, the component (A) contains at least one 5-membered cyclic carbonate group. Preferred component (A) are chloride, bromide or iodide of 4- (trimethylammoniummethyl)-1,3-dioxolane-2-one, 4-(N-benzyl-N,N-dimethylammoniummethyl)-1,3-dioxolane-2-one and the tetracarbonate made starting from the tetraglycidylether of metaxylylenediamine.

Such 5-membered cyclic carbonate compounds are very desirable because they can be easily prepared starting from cheap epoxides in a reaction with carbondioxide. A reaction of which is already known that it can be catalysed by a lithiumsalt : ref Kihara, N., Hara, N., Endo, T.; J. Org Chem., 1993, 58, 6198-6202.

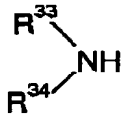
Examples of useful epoxide compounds include, without limitation, epichlorohydrin, epibromohydrin, 2,3-epoxypropyl methacrylate, trans-2,3-epoxy-1,3-diphenyl-1-propanone, (brominated) bisphenol A diglycidyl ether, methyl glycidate.

According to the invention, component (A) may be prepared by reacting compounds (A) where the electrophilic group Y is chloride or bromide or iodide with a nucleophilic compound such as a tertiary (trialkyl)amine, or a trialkyl phosphine or phosphite. A catalyst may eventually be

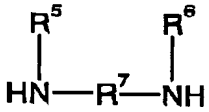
used for accelerating the reaction. These catalysts are selected between quaternary ammonium and phosphonium salts such as tetra-n-butylammonium chloride, tetramethylammonium bromide, benzyltrimethylammonium chloride, tetra-n-butylphosphonium bromide and the like.

Preferably, the component (B) contains at least one nucleophilic function X which is an amino group.

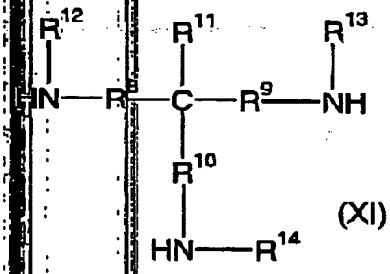
Preferably, component (B) is an amine of formula (IX), (X), (XI) or (XII)



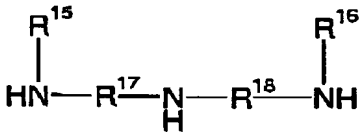
(IX)



(X)



(XI)



(XII)

wherein

R^{33} is an alkyl, optionally substituted by hydroxy, tertiary amine and/or aryl, and optionally containing from 1 to 20 ether bridges and/or from 1 to 3 tertiary amine bridges,

R^{34}, R^5, R^6, R^{12}, R^{13}, R^{14}, R^{15} and R^{16} are, independently, chosen from the group of

- hydrogen, and
- alkyl, optionally substituted by hydroxy, tertiary amine and/or aryl, and optionally containing from 1 to 8 ether bridges and/or from 1 to 3 tertiary amine bridges,
- with the proviso that, respectively, R^{33} and R^{34}, R^5 and R^6, R^{12} and/or R^{13} and/or R^{14}, R^{15} and R^{16} may be linked together in order to form a ring,

R^7, R^8, R^9, R^{10}, R^{17} and R^{18} are, independently, chosen from alkylene, alkenylene, arylene and aralkylene chains which may contain from 1 to 8 ether bridges and/or from 1 to 3 tertiary amine bridges,

R^{11} is hydrogen or alkyl.

In the amines of formula (IX) R^{33} is preferably an alkyl, optionally substituted by hydroxy, tertiary amine and/or aryl, and optionally containing from 1 to 20 ether bridges. Most preferably, R^{33} is chosen from the group of alkyl comprising up to 10 carbon atoms, optionally

substituted by one hydroxy or tertiary amine and/or optionally containing one or two ether bridges. Non-limiting examples are R^{33} substituents chosen from the group of n-propyl, isopropyl, n-butyl, isobutyl, sec-butyl, tert-butyl, n-hexyl, n-octyl, 2-ethylhexyl, isononyl, cyclopentyl, cyclohexyl, 2-methylcyclohexyl, N,N-(di-tert-butyl)ethyl, benzyl, 2-(2-hydroxyethoxy)ethyl, 5-hydroxypentyl, 2-hydroxyethyl, 2-hydroxypropyl, 3-hydroxypropyl, 3-(diethylamino)propyl, 2-(diethylamino)ethyl, 4-methyl-4-(diethylamino)butyl, 2-((di-tert-butyl)amino)ethyl, 3-(dimethylamino)propyl, 2-methoxyethyl, 2-ethoxyethyl, 3-methoxypropyl, 2-methoxyisopropyl, 3-ethoxypropyl, 3-isopropoxypropyl, 3-(2-methoxyethoxy)propyl, 3-(2-ethylhexyloxy)propyl, $CH_3O(CH_2CH_2O)_6$-$(CH_2CHR$-$O)_{10}$-CH_2-$CH(CH_3)$- wherein R is H or CH_3 in a proportion of 1:9, ethyl, methyl, 1,2-dimethylpropyl.

In the amines of formula (IX) R^{34} is preferably chosen from the group of hydrogen and alkyl, optionally substituted by hydroxy, tertiary amine or aryl, and optionally containing from 1 to 8 ether bridges. Most preferably, R^{34} is chosen from the group of hydrogen and alkyl comprising up to 10 carbon atoms, optionally substituted by one hydroxy or tertiary amine and/or optionally containing one or two ether bridges. Non-limiting examples are R^{34} substituents chosen from the group of hydrogen, ethyl, n-propyl, isopropyl, n-hexyl, methyl, tert-butyl, n-butyl, isobutyl, n-octyl, 2-ethylhexyl, 1,2-dimethylpropyl, cyclohexyl, 2-hydroxyethyl, 2-hydroxyisopropyl, 3-hydroxypropyl, 2-methoxyethyl, 3-(dimethylamino)propyl.

In the amines of formula (X), (XI) and (XII) R^5, R^6, R^{12}, R^{13}, R^{14}, R^{15} and R^{16} are preferably, independently, chosen from the group of hydrogen and alkyl comprising up to 10 carbon atoms, most preferably up to 6 carbon atoms.

In the amines of formula (IX), (X), (XI) and (XII) R^{33} and R^{34}, R^5 and R^6, R^{12} and/or R^{13} and/or R^{14}, R^{15} and R^{16}, respectively, may be linked together in order to form a ring. In this case, these substituents are preferably linked so that they form an alkylene chain comprising from 2 to 7 carbon atoms, and optionally containing 1 or 2 ether bridges. In case of R^{33} and R^{34}, this alkylene chain is preferably such that a 5 to 7-membered ring is formed, for example a pyrolidine ring, a piperidine ring or a morpholine ring, which may further be substituted by alkyl groups. In case of R^6 and R^6, this alkylene chain is preferably such that a 5 to 7-membered ring is formed, for example piperazine, which may further be substituted by alkyl groups.

In the amines of formula (X) R^7 is preferably chosen from the group of alkylene and aralkylene chains, containing up to 20 carbon atoms and which may contain from 1 to 8 ether bridges and/or from 1 to 3 tertiary amine bridges. Most preferably, R^7 is chosen from the group of ethylene, 1,2-propylene, trimethylene, hexamethylene, 2,2-dimethylpropylene, 1-methyltrimethylene, 1,2,3-trimethyltetramethylene, 2-methyl-pentamethylene, 2,2,4-(or 2,4,4-)trimethylhexamethylene, metaxylylene, 3,5,5-trimethylcyclohexyl-1-ene-3-methylene, bis(cyclohexyl-4-ene)methane, bis(4-methylcyclohexyl-3-ene)methane, cyclohexyl-1,3-ene.

cyclohexyl-1,4-ene, 1,4-bis(propoxyl-3-ene)butane, N,N-bis(trimethylene)methylamine, 3,6-dioxaoctylene, 3,8-dioxadodecylene, 4,7,10-trioxatridecylene, poly(oxytetramethylene), poly(oxypropylene) with 2 to 15 1,2-propylene oxide units, poly(oxypropylene-co-oxyethylene) with 2 to 15 propylene oxide and 2 to 15 ethylene oxide units, 2,2-dimethylpropylene.

In the amines of formula (XI) R^8, R^9, R^{10} are preferably, independently, chosen from the group of alkylene, optionally containing from 1 to 8 ether bridges. Most preferably R^8, R^9, R^{10} are chosen from alkylene comprising up to 15 carbon atoms and containing up to 5 ether bridges.

In the amines of formula (XII) R^{17} and R^{18} are preferably, independently, chosen from the group of alkylene. Most preferably R^{17} and R^{18} are chosen from alkylene comprising up to 6 carbon atoms.

In the amines of formula (XI) R^{11} is preferably hydrogen or an alkyl containing from 1 to 4 carbon atoms.

Amines of formula (IX), (X), (XI) and (XII) are known in the art. Amines of formula (IX) which are particularly useful in the process according to the invention are n-propylamine, isopropylamine, n-butylamine, isobutylamine, sec-butylamine, tert-butylamine, 3-methylbutylamine, n-hexylamine, n-octylamine, 2-ethylhexylamine, isononylamine, cyclopentylamine, cyclohexylamine, 2-methylcyclohexylamine, N,N-(di-tert-butyl)ethyleneamine, benzylamine, 2-(2-aminoethoxy)ethanol, 5-aminopentanol, ethanolamine, 1-aminopropan-2-ol, 3-amino-1-propanol, 3-(diethylamino)propylamine, 2-(diethylamino)ethylamine, 1-methyl-4-(diethylamino)butylamine, 2,2-(di-tert-butylamino)ethylamine, 3-(dimethylamino)propylamine, 2-methoxyethylamine, 2-ethoxyethylamine, 3-methoxypropylamine, 1-methoxyisopropylamine, 3-ethoxypropylamine, 3-isopropoxypropylamine, 3-(2-methoxyethoxy)propylamine, 3-(2-ethylhexyloxy)propylamine, polyoxyalkylene amines such as α-oxymethyl-ω-(2-propylamino)-poly(oxypropylene-co-oxyethylene) with an average number of 1,2-propylene oxide units of 9 and an average number of ethylene oxide units of 7, also known as Jeffamine® M-600 (manufactured by Hunstman), diethylamine, di-n-propylamine, diisopropylamine, di-n-hexylamine, N-methylbutylamine, N-ethylbutylamine, di-n-butylamine, diisobutylamine, di-n-octylamine, bis(2-ethylhexyl)amine, N-ethyl-1,2-dimethylpropylamine, dicyclohexylamine, cyclohexylmethylamine, cyclohexylethylamine, N-methylbenzylamine, 2-methylaminoethanol, 2-ethylaminoethanol, 2-butylaminoethanol, diethanolamine, diisopropanolamine, 3-(2-hydroxyethyl)aminopropanol, bis(2-methoxyethyl)amine, bis(3-dimethylaminopropyl)amine, pyrolidine, piperidine, morpholine, 2,6-dimethylmorpholine.

Amines of formula (X) which are particularly useful in the process according to the invention are ethylenediamine, 1,2-propylenediamine, trimethylenediamine, hexamethylenediamine, 2,2-dimethylpropane-1,3-diamine, 1-methyl-1,3-propanediamine,

1,2,3-trimethyl-1,4-butanediamine, 2-methyl-1,5 diaminopentane, 2,2,4-(or 2,4,4-)trimethylhexamethylene diamine, metaxylylenediamine, 1-amino-3-aminomethyl-3,5,5 trimethylcyclohexane (isophorone diamine), bis-(4-aminocyclohexyl)-methane, bis-(4-amino-3-methyl-cyclohexyl)-methane, 1,3- cyclohexanediamine, 1,4-cyclohexanediamine, 1,4-Bis(3-aminopropoxy)butane diamine, N,N-bis(3-aminopropyl)methylamine, triethyleneglycol diamine, 3,3'-(butane-1,4-diylbis(oxy))bispropaneamine, 4,7,10-trioxatridecan-1,13-diamine, polyoxyalkylene diamines such as α-amino-ω-(2-butylamino)-poly(oxytetramethylene), α-amino-ω-(2-propylamino)-poly(oxypropylene) with an average number of 1,2-propylene oxide units of 2.6, also known as Jeffamine® D-230 (manufactured by Hunstman), α-amino-ω-(2-propylamino)- poly(oxypropylene) with an average number of 1,2-propylene oxide units of 5.6, also known as Jeffamine® D-400 (manufactured by Hunstman), α-amino-ω-(2-propylamino)-poly(oxypropylene-co-oxyethylene) with an average number of 1,2 propylene oxide units of 2.5 and ethylene oxide units of 8.5, also known as Jeffamine® ED-600 (manufactured by Hunstman), 2,2-dimethyl-1,3-propanediamine, N,N'-di-tert-butyl-ethanediamine, N,N'-dimethylhexyl-1,6-diamine, piperazine, 1,6-diamino-trimethylhexane, N,N'-dimethyl-1,3-propanediamine and 2,5-dimethylpiperazine.

Amines of formula (XI) that are particularly useful in the process according to the invention is propoxylated trimethylopropane triamine with an average number of number of 1,2-propylene oxide units of 5.3, also known as Jeffamine® T-403 (manufactured by Hunstman).

Amines of formula (XII) that are particularly useful in the process according to the invention are diethylenetriamine, N,N-dimethyldipropylenetriamine, bis(hexamethylene)triamine.

In an embodiment of the invention, compound (B) contains only one primary or secondary amino group.

In other preferred embodiments of the invention, component (B) is a compound containing at least two primary or secondary amino groups. This permits to obtain dimers, oligomers and even polymers when reacted with a component (A) containing at least two linked carbonate rings.

Especially preferred are amines chosen among: cyclohexylamine, N-methylbutylamine, N-methylbenzylamine, piperidine, piperazine, morpholine, benzylamine, diethylenetriamine, ethanolamine, diethanolamine and polyoxyalkylene amines and diamines.

The component (B) can also be chosen among hydrazo compounds such as : hydrazine, mono, di and tri-substituted hydrazines H_2N-NHR^{29}, $R^{29}H_2N-NR^{29}R^{30}$, $R^{29}HN-NHR^{30}$, $R^{29}HN-NR^{30}R^{35}$ wherein R^{29}, R^{30} and R^{35} are as defined for R^{33}.

The component (B) can also be chosen among hydroxy compounds such as (polyfunctional) alcohols, for example methanol, ethanol, propanol, isopropanol, butanol,

phenol, butanediol, hexanediol, trimethylolpropane, pentaerythritol, glucose, (poly)hydroxy functional oligomers or polymers such as polyesters, polyethers, polycarbonates, polyurethanes, polybutadiene, acrylic polyol, polysiloxanes, starch and the like.

It was found that the reaction temperature between compounds (A) and (B) is not critical and can be comprised between 0 and 120°C. The amount of component (A) and component (B) in the process according to the invention is preferably such that the molar ratio of cyclic carbonate groups to nucleophilic groups X is from 0.5 to 2. In case that a component (A) comprising only one cyclic carbonate group and/or a component (B) comprising only one nucleophilic group X is used, the ratio of amount of such components is preferably such that an almost equivalent ratio of cyclic carbonate groups to nucleophilic groups X is obtained.

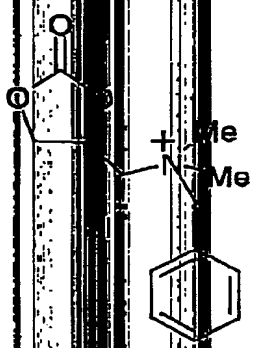
The reaction can be made with or without solvent. When a solvent is used, it is preferably chosen among alcohol, ether, ester, dimethylformamide, dimethylsulfoxide, N-methylpyrolidone and water.

The invention also extends to a polymeric composition containing a nonisocyanate polyurethane polymer comprising urethane functions -NCOO- which contain ternary-substituted nitrogen and bear an hydroxy group in beta-position (betahydroxyurethane).

The invention will now be illustrated by examples.

Example 1 :

Reaction of N-benzyldimethylamine with 4-chloromethyl-1,3-dioxolan-2-one



In a 200 ml flask were added N-benzyldimethylamine (60 gram), 4-chloromethyl-1,3-dioxolan-2-one (50 gram) and catalyst tetrabutylammoniumiodide. (2 gram) The mixture is heated to 100°C. The reaction is followed by potentiometrically titrating the remaining amine. When the reaction is finished the precipitate is filtered, washed with diethylether and dried, affording 20 grams of product . The final product has a carbonate content of 3.6 mmol carbonate/gram (theory 3.7 mmol/gr) and a chlorine content of 12 % (theory 13%)

Example 2 and comparative example :

Example 2 and comparative example were run by the same general procedure.
For example 2 : 0.136g (0.0005 mole) of the ammoniumcarbonate prepared in example 1 was dissolved into 4 ml DMSO d6. Then 0.06g (0.0026 M) 2-methyl-1,5-pentanediamine is added and mixed together, just prior to taking the NMR spectrum. 600µL of this solution was transferred to the NMR tube.
For the comparative example the same procedure was used except that instead of the carbonate of example 1 0.044g (0.0005 mole) of ethylenecarbonate was used
The NMR-spectra were taken on a "Bruker" 400 MHz spectrometer
The integrated NMR-values observed and used for calculation the resulting urethane are located at δ = 7.55 ppm and δ = 5.6 ppm for example 2, resp. the phenyl group of the carbonate of this invention and the CH2-O-CO-NH group of the resulting urethane, and δ = 4.95 ppm and δ = 4.5 ppm for the comparative example, resp. the (CH2)2 signal of ethylenecarbonate and the CH2O-CO-NH group of the resulting urethane.
Table 1 shows the decrease in cyclic carbonate concentration for example 2. For comparison, the same reaction was run but the carbonate of this invention was replaced with ethylenecarbonate. The time given is taken from the time of initial mixing of the components.

Table 1

Example 2 Carbonate of this invention		Comparative example Ethylenecarbonate	
Time (min)	Relative fraction of remaining carbonate	Time (min)	Relative fraction of remaining carbonate
6	90	12	98.9
60	65	60	97.4
960	30	1200	94.3
1560	25	1800	91.3
2460	19	2670	86.4

Example 3

0.05 gram of the carbonate of example 1 is added to 1 ml of methanol. The reaction is monitored with NMR. The remaining fraction of carbonate is listed in table 2. As the characteristic signal of the carbonate of example 1 at δ = 5.6 ppm is disappearing a new singlet at δ = 3.1 ppm appears. The cyclic carbonate reacts with the methanol and forms a linear carbonate as is evidenced by the NMR.

Table 2

Example 3 Carbonate of the invention	
Time (min)	Relative fraction of remaining carbonate
0	1.0
60	.79
120	.60

Example 4 :

Example 4 was run by the same general procedure as example 2.

0.136g (0.0005 mole) of the ammoniumcarbonate prepared in example 1 was dissolved into 4 ml deuterated methanol. Then 0.0300g (0.0026 mole) 2-methyl-1,5-pentanediamine is added and mixed together, just prior to taking the NMR spectrum. 600µL of this solution was transferred to the NMR tube.

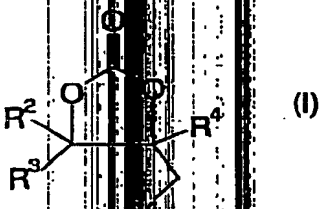
The NMR-spectra were taken on a "Bruker" 300 MHz spectrometer

After 5 minutes the NMR spectrum shows that the characteristic signal for the ammonium carbonate has almost completely disappeared, indicating an extremely fast reaction.

CLAIMS

1. Process of forming an organic compound, wherein

(a) a component (A) containing at least one cyclic carbonate group having the general formula (I):



(I)

wherein:

R^2, R^3 and R^4 are, independently, chosen from hydrogen, aromatic radical, alkyl or alkenyl which contains from 0 to 8 ether bridges, and R^2 and/or R^3 and/or R^4 may be substituted by one or more alkyl, alkenyl, aromatic radical, hydroxyl group, cyclic carbonate group of formula (I), and wherein Y is an electrophilic group selected from ammonium and phosphonium, eventually substituted by alkyl groups themselves eventually substituted by aromatic radicals, and wherein each R^2 and/or R^3 and/or R^4 may be replaced by an Y group.

(b) is reacted with a component (B) containing at least one reactive nucleophilic function X wherein each X is, independently, chosen from a primary amino or hydrazo, secondary amino or hydrazo, thiol, hydroxy, and/or oxhe,

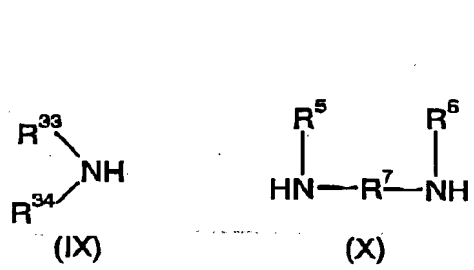
(c) to form an organic compound (C) containing at least one unit of the general formula (II): -X-CO-O-.

2. Process according to claim 1, wherein component (A) contains at least two carbonate cycles.

3. Process according to any of claims 1 or 2, wherein component (A) is chosen from 4-(trimethylammoniummethyl)-1,3-dioxolan-2-one, 4-(N-benzyl-N,N-dimethylammoniummethyl)-1,3-dioxolan-2-one and the tetracarbonate made starting from the tetraglycidylether of metaxylylenediamine.

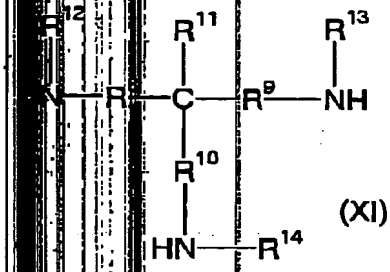
4. Process according to any preceding claim, wherein component (B) contains at least one nucleophilic function X which is an amino group.

5. Process according to claim 4, wherein component (B) is an amine of formula (IX), (X), (XI) or (XII)

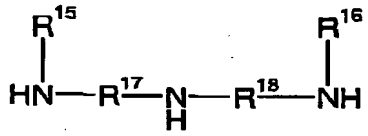


(IX)

(X)



(XI)



(XII)

wherein

R^{33} is an alkyl, optionally substituted by hydroxy, tertiary amine and/or aryl, and optionally containing from 1 to 20 ether bridges and/or from 1 to 3 tertiary amine bridges,

R^{34}, R^5, R^6, R^{12}, R^{13}, R^{14}, R^{15} and R^{16} are, independently, chosen from the group of

- hydrogen, and
- alkyl, optionally substituted by hydroxy, tertiary amine and/or aryl, and optionally containing from 1 to 8 ether bridges and/or from 1 to 3 tertiary amine bridges,
- with the proviso that, respectively, R^{33} and R^{34}, R^5 and R^6, R^{12} and/or R^{13} and/or R^{14}, R^{15} and R^{16} may be linked together in order to form a ring,

R^7, R^8, R^9, R^{10}, R^{17} and R^{18} are, independently, chosen from alkylene, alkenylene, arylene and aralkylene chains which may contain from 1 to 8 ether bridges and/or from 1 to 3 tertiary amine bridges,

R^{11} is hydrogen or alkyl.

6. Process according to claims 4 or 5, wherein component (B) contains at least two primary or secondary amino groups.

7. Process according to claims 4 to 6, wherein component (B) is an amine chosen amongst cyclohexylamine, N-methylbutylamine, N-methylbenzylamine, piperidine, piperazine, morpholine, benzylamine, diethylenetriamine, ethanolamine, diethanolamine and polyoxyalkylene amines and diamines.

8. Process according to any preceding claim wherein the reaction temperature is comprised between 0 and 120°C.

9. Process according to any preceding claim wherein the amount of component (A) and component (B) are such that the molar ratio of cyclic carbonate groups to nucleophilic groups X is from 0.5 to 2.

10. Process according to any preceding claim wherein the reaction is made in a solvent chosen among: alcohol, ether, ester, dimethylformamide, and water.

11. Process according to any preceding claim wherein component (A) is prepared by reacting compounds (A) where the electrophilic group Y is chloride or bromide or iodide with a nucleophilic compound such as a tertiary trialkyl amine, or a trialkyl phosphine or phosphite.

ABSTRACT

The present invention relates to a process wherein a cyclic carbonate compound bearing an electrophilic group is reacted with a compound containing a nucleophilic group, especially an amine group. Such reactions permit to obtain urethane groups useful in polymer preparation, such as polyurethanes, or other urethane-containing polymers.

FR/FD

22.31.EP

UCB S.A./N.V. - Département Propriété Intellectuelle - Allée de la Recherche 60, B-1070 Bruxelles
Intellectuele Eigendom Departement - Researchdreef 60, B-1070 Brussel
Intellectual Property Department - Allée de la Recherche 60, B-1070 Brussels

FACSIMILE & REGISTERED MAIL

EUROPEAN PATENT OFFICE
D- 80298 MÜNCHEN (Germany)

Our ref.: Case 22.31.EP
IPD/0304-115

Brussels, April the 24th, 2003.

Your ref.:

Re: Filing of a new European Patent Application.

Dear Sirs,

Please find herewith enclosed the following documents, necessary for filing a new European Patent Application:

- Form 1001 « Request for grant of a European patent » :
- Form 1002 "Designation of Inventor"
- General Authorization No. 40404 ;
- 1 paper copy of description (12 pages), claims (3 pages) and abstract (1 page).

Best regards,

François ROELANTS

Enclosures (as mentioned)

2231_EPoo.doc